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Efficiency of some silane coupling agents and of the method of their application in polyester resin concrete

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The effects of two silane coupling agents, γ-methacryloxy propyl trimethoxy silane and γ-amino propyl triethoxy silane, on the compressive strength of polyester resin concrete (PC) is studied by using two methods of application of the coupling agent, namely by (a) pre-treatment of the aggregates in an aqueous solution of the silane, (b) by adding the silane to the resin as an integral blend additive. The performance of the two methods, evaluated in terms of gain in the compressive strength, is compared. Method (b), which is preferable due to its convenience, showed comparable performance to method (a) only at the optimum level of loading of the coupling agent. Changes in X-ray diffraction of "PC with coupling agent" prepared by method (b) were similar to those in silane-treated sand particles, which support the migration theory of the coupling agent reported in the literature. Grain size analysis of silane-treated sand showed evidence of better aggregation in the presence of one coupling agent as compared to the other.

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1. Introduction

Polymer concretes, where polymeric resins are used as the binder of the sand and aggregates, have considerably better mechanical properties than the conventional cement concrete. Use of silane coupling agents results in considerable improvement of the mechanical properties of these materials owing to the strengthening of the bonding between the binder and the aggregates [1, 2].

Two different methods of application of the silane coupling agent are suggested [3], namely, method (a) pre-treatment of the aggregates with aqueous solution of the silane coupling agent, and method (b) addition of the silane coupling agent to the resin–aggregate mix as an integral blend additive. Both these methods have their own merits and demerits. Method (a), which is apparently more efficient because the coupling agent is applied at the most appropriate site (i.e. the aggregate surface), involves wastage of the coupling agent, as part of it outflows with the treating medium. Method (b) has the merit that it does not involve the pre-treatment step and is thus preferable for mass production of the polymer concrete. The demerit of method (b) is almost similar to that of method (a), as only part of the coupling agent added might reach the aggregate–resin interface. However, there is evidence in the literature [4–5], where it is stated that the silane coupling agent migrates from the bulk of the resin to its surface. This also does not rule out the possibility of unused coupling agent being left in the system, since the total surface of the resin would not necessarily be in contact with the aggregates in these materials which also have voids.

In this paper we present a comparative evaluation of the two methods of application of the coupling agent, using the silane coupling agents, on polyester-resin concrete (PC). The two silane coupling agents had the commercial and chemical names Dynasil MEMO (γ-methacryloxy propyl trimethoxy silane), and Dynasil AMEO (γ-amine

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propyl triethoxy silane) respectively, supplied by Dynamit Nobel Chemicals, Troisdorf-Oberlar, FRG. The former coupling agent was of a reactive type while the latter coupling agent was of a non-reactive type, on the basis of their reactivity with the polyester resin. However, in the case of the nonreactive type, the possibility of secondary bonds is not ruled out.

The relative efficiency of the two coupling agents and of the two methods of application of coupling agent are discussed on the basis of the comparison of compressive strength at identical conditions. Grain size analysis and X-ray diffraction data which provide support for the better adhesion effect of one silane over the other are also presented. Before moving onto the results and discussion, a brief discription of the materials and the experimental procedures are given.

2. Materials and methods

Commercial unsaturated polyester resin (general purpose grade), supplied by Crystic (India) Pvt. Ltd, was used as the binder with 50% solution of methyl ethyl ketone peroxide in dimethyl phthalate as catalyst and 1% styrene solution of cobalt naphthenate as an accelerator.

The coarse aggregates used were crushed quartzite aggregates with maximum size 10 mm and specific gravity 2.72. Siliceous sand (locally known as Badarpur sand), passing through a BSS 14 sieve (1.18 mm) and retained on a BSS 100 sieve (150 μm) and specific gravity 2.6 were the fine aggregates used.

PC samples were prepared by mixing 12 wt % resin containing catalyst and accelerator with the aggregate mix of appropriate grading [7, 8] (grading modulus = 6.42 mm^{-1}, mean diameter = 4.12 mm and fineness modulus = 4.40). The silane coupling agent in method (b) was added to the resin mix as an integral blend additive in varying proportions from 0.3 to 1.5 wt % of the binder. In method (a) the aggregates were treated with 0.5% aqueous solution of the silane coupling agent and then dried at 105° C for 4 h. The total silane content of the treatment bath amounted to 1 wt % of the binder. The homogenized resin–aggregate mix was compacted in cylindrical moulds of 50 mm diameter and 100 mm height. After room temperature curing for 24 h, the cast specimens were demoulded and further cured at 70° C for 24 h. The composition and nomenclature of the various samples studied are shown in Table I.

Grain size analysis was carried out on fine sand, passing through a BSS 200 sieve (75 μm). The sand was slurried with 0.5% solution of the respective silane coupling agent in water for 1 h at room temperature. The entire mixture was then dried for 4 h in an air oven at 105° C, so that the agglomerates were broken up. Grain size measurements were done on pure sand and silane-treated sand by using a hydrometer, calibrated in specific gravity [9].

TABLE I Description of the samples.

Sample number	Sample nomenclature	Composition (wt %)		Method of application of coupling agent*
		Aggregate	Resin mix	
1	Sand	100	–	–
2	Sand–MEMO	100	–	a
3	Sand–AMEO	100	–	a
4	PC	88	12	–
5	PC–MEMO	88	12	a
6	PC–AMEO	88	12	a
7	PC–0.3† MEMO	88	12	b
8	PC–0.5 MEMO	88	12	b
9	PC–1.0 MEMO	88	12	b
10	PC–1.5 MEMO	88	12	b
11	PC–0.3 AMEO	88	12	b
12	PC–0.5 AMEO	88	12	b
13	PC–1.0 AMEO	88	12	b
14	PC–1.5 AMEO	88	12	b

*a – pre-treatment of aggregates with aqueous solution of the coupling agent. b – addition of the coupling agent as an integral blend additive.

† – numbers indicate the fraction in wt % of the coupling agent with respect to the resin.

X-ray diffraction measurements were done on powder samples of pure sand, silane-treated sand, PC without any coupling agent, and PC with the coupling agents. Diffractograms in the range $2\theta = 15^\circ$ to 60° were recorded on a Philips Norelco X-ray diffractometer using Cu$K\alpha$ radiation (wavelength, $\lambda = 0.154\,18$ nm). All diffractograms were recorded on identical settings of the instrument.

Compressive strengths of the cast cylindrical PC samples were measured on Avery Compression Tester at the loading rate of 2400 kg min^{-1}. More than three samples were tested in each case and the variation of the results were between 5 and 10% in all cases.

3. Results and discussion

3.1. Compressive strength

Compressive strengths of the various PC samples are shown in Table II. The compressive strength of PC with coupling agent (samples 5 to 14) is higher than that of PC without coupling agent (sample 4). Samples 5 and 6, which were prepared by pre-treating the aggregates with coupling agent, show higher compressive strengths than the samples prepared by adding the coupling agent as an integral blend additive. In the latter case (samples 7 to 14) a variation in compressive strength with coupling agent content is observed, and it was similar for the two types of the coupling agents. Maxima in compressive strength were reached around 0.5 to 1.0 wt% coupling agent content. These maximum values achieved by the method of pre-treatment (i.e. samples 5 and 6) of the aggregates with respective coupling agents. The observed lowering of compressive strength with increasing coupling agent content beyond the 1.0% level suggests that the direct addition of silane to the resin mix beyond a certain appropriate amount produces an adverse effect on the strength of the PC. In the case of an excess amount of silane (added to the system over that required), a deposition of a thick layer of oligomeric silanols occurs, which will form a distinct interphase between the resin matrix and aggregate [10]. The coupling agent sitting in the bulk of the resin might react with its constituents and reduce the effective cross-linking density of the polymer matrix. Thus it may be stated that there occurs an optimum level for coupling agent content, when it is applied by the method of direct addition to the resin aggregate mix.

TABLE II Compressive strength of the various PC samples

Sample number	Sample	Compressive strength (kg cm^{-2})
4	PC	420
5	PC–MEMO	575
6	PC–AMEO	510
7	PC–0.3 MEMO	465
8	PC–0.5 MEMO	530
9	PC–1.0 MEMO	540
10	PC–1.5 MEMO	495
11	PC–0.3 AMEO	431
12	PC–0.5 AMEO	445
13	PC–1.0 AMEO	475
14	PC–1.5 AMEO	465

Furthermore, it is apparent from these results that, at all other identical conditions, the improvement in compressive strength is greater in the case of coupling agent MEMO than coupling agent AMEO. This coincides with the reactive and non-reactive nature of these coupling agents with respect to polyester resin. Our previous work [11] on infrared spectroscopy and scanning electron microscopy also gave better support to interfacial bonding in this system with coupling agent MEMO than with AMEO.

3.2. Grain size distribution analysis

Grain size distribution analysis has been widely used in the analysis of soils by separating them into fractions of different size by either sieve analysis or sedimentation (or hydrometer) method [12–15]. The grain size distribtion is commonly represented by a curve with the per cent weight of particles smaller than a given diameter plotted as a function of the mean diameter [12]. In the hydrometer method, used in the present study, the percentage of particles finer (N%) than a given mean diameter (D) is calculated by the specific gravity of the suspension at various time intervals, and the mean diameter is calculated from the velocity of fall and the specific gravity of the suspension and the particles [12, 13].

Grain size distribution curves of these samples of untreated sand and the sand treated with silanes MEMO and AMEO are shown in Fig. 1. The distribution curve of untreated sand (sample 1) extends up to an upper limit of mean diameter which is quite consistent with the sieve size (i.e. 75 μm) used for the initial selection of the sample. The silane treatment of this sand sample resulted in an overall downward displacement of the grain size distribution curve (compare curves for samples 2 and 3 with that of sample 1 in Fig. 1). This shift-

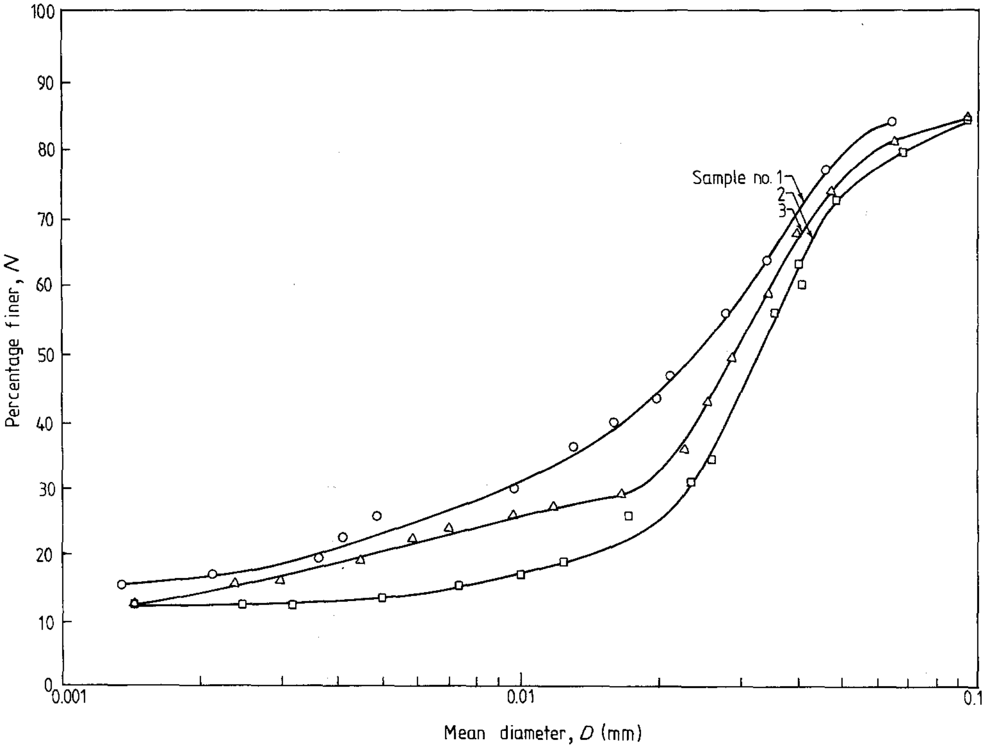

Figure 1 Grain size analysis data of the various sand samples: 1 – pure sand, 2 – sand treated with MEMO, 3 – sand treated with AMEO.

ing of the grain size distribution curve indicates the increase of grain size in all size ranges of the sand particles on silane treatment. Such an increase in grain size may occur due to the coating of silane on the sand surface and cluster formation of finer particles owing to the adhesion provided by the silane. It is further noteworthy that the increase of grain size is greater in the case of the silane MEMO (sample 2) than silane AMEO (sample 3), which supports not only the greater adhesion in the case of MEMO as compared with AMEO but also confirms that the observed increase in grain size is an effect of the silane treatment. Similar effects on grain size distribution are reported [14, 15] in the case of iron oxide coating on the mineral surface which binds them into coarse aggregates. Removal of iron oxide by chemical means resulted in a decrease in grain size [14, 15].

3.3. X-ray diffraction

X-ray diffraction studies on laterite soil samples reported by other authors [12, 14, 15] have shown interesting behaviour. The occurrence of a previously absent quartz peak (0.335 nm) after the removal of sesquioxides also produced the increase in sharpness of some other peaks [12, 14]. However, it was not possible to quantify the degree of sesquioxide coatings from the X-ray diffraction patterns [12, 14, 15]. X-ray diffraction studies on the present samples of sand and PC showed somewhat similar effects on certain peaks. The experiments were conducted under identical scanning time and incident beam intensity for all samples, and the reproducibility of the effect (to be described below) was confirmed by repeating the experiments.

X-ray diffractograms (radial scans of intensity against diffraction angle 2θ) of the various samples, listed in Table I, are shown in Fig. 2. The prominent peaks of crystalline structure of silica are identified from the literature [16], as marked in the figure. The (101) reflection, occurring at $2\theta = 26.4°$, is the most intense in all the cases. Comparison of these diffraction patterns for the various samples shows some systematic variations in the intensities of several reflections, e.g. (100), (102), (112), (103) and (211) reflections. Variations in peak-widths are apparently too low to be distinguished, hence we confine the present discussion to the variation of intensities alone. Since it is difficult in the powder samples to maintain

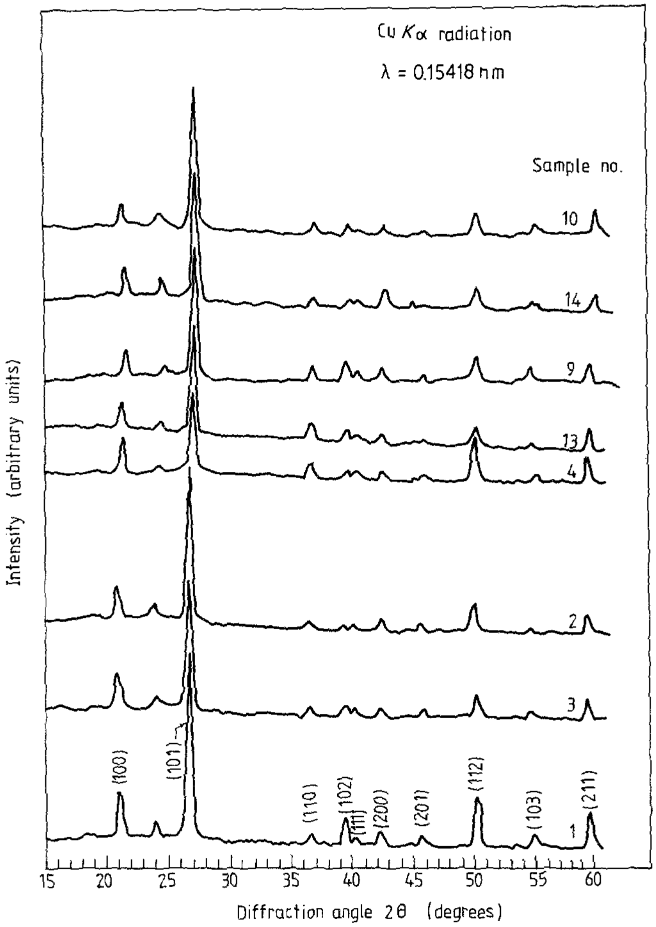

Figure 2 X-ray diffractograms of the various samples.

constant volume of the sample in the X-ray beam for each different sample mounting, the intensities of any given reflection in different samples were compared after normalization of the diffraction patterns to constant height of the most intense reflection (101). Such a normalization is automatically incorporated when one compares the ratio of peak height of any given reflection with the peak height of the (101) reflection. This normalization is somewhat approximate compared to the normalization of the area under the diffraction pattern, but may not be too drastic for the present case owing to the extremely high intensity of only one reflection, namely (101) in the diffraction pattern.

The relative peak heights, h_{100} and h_{112}, of two peaks (100) and (112) with respect to the (101) reflection are shown in Table III for the various samples studied. The trends of variation in these results are almost identical in both the reflections (100) and (112). The values may be taken for qualitative comparison owing to low intensities of the peaks involved.

The relative intensities (h_{100} and h_{112}) are higher for untreated sand than for the sand treated with silanes MEMO or AMEO (compare samples 1, 2 and 3). However, the difference between sand treated with MEMO and sand treated with AMEO was too low to be emphasized (compare samples 2 and 3). Similarly, the difference in these quantities for PC (sample 4) and untreated sand (sample 1) is not appreciable. In the case of PC with silane coupling agent (samples 9, 10, 13 and 14) the rela-

TABLE III Relative peak intensity ratios of (100) and (112) reflections in the X-ray diffraction patterns of various samples

Sample number	Sample nomenclature	h_{100}	h_{112}
1	Sand	0.238	0.284
2	Sand–MEMO	0.218	0.188
3	Sand–AMEO	0.197	0.194
4	PC	0.252	0.310
9	PC/1.0 MEMO	0.178	0.194
10	PC/1.5 MEMO	0.149	0.159
13	PC/1.0 AMEO	0.162	0.186
14	PC/1.5 AMEO	0.165	0.160

tive intensities of both these peaks are lower as compared to that of PC without coupling agent (sample 4).

The almost equal values of h_{100} (or h_{112}) for untreated sand (sample1) and the PC without silane coupling agent (sample 4), suggest that the resin coating on sand produces an insignificant change in the intensities of these diffraction peaks as compared to the change produced by silane coating on the sand (samples 2 and 3). Furthermore, the PC samples containing silane coupling agent (samples 9, 10, 13 and 14) show lower values of h_{100} (or h_{112}), in the case of both the silanes, like the effect observed in silane-treated sand *vis-à-vis* untreated sand. This effect was greater at the 1.5% level of silane content (samples 10 and 14) than at the 1.0% level (samples 9 and 13) for both the silanes, which seems to support the concept of the formation of a layer of silanol oligomers around the aggregate surface at the excess silane loading suggested in the literature [10].

The origin of the observed change of peak heights in the X-ray diffraction pattern seems difficult to ascertain for these diffraction patterns where peak broadening is not measurable. Cluster formation of aggregates on adhesion through the silane coupling agent might give rise to some peak broadening which may become apparent as a decrease in peak height. Another possible explanation may be that the decrease of peak heights might be due to the silane coating which is an effect similar to that reported [12, 14] in the case of soils where the removal of iron oxide coating increased the intensities and sharpness of certain peaks (or, in other words, the peaks were broad and less intense in the presence of iron oxide coating). The third possible explanation, namely that the silane coating is degraded to crystalline silica by the X-ray beam, seems less likely because the exposure times used were quite short (less than 15 min for the toal scan over the measured range of 2θ).

Interestingly, these results suggest that, whatever the origin of the observed effect, the effect of silanes in the case of PC samples was similar to what is seen in silane-treated sand. Since these PC samples were prepared by the integral blend additive method of the application of the silane, these results provide some indirect evidence of the migration of the silane coupling agent from the bulk of the resin to the aggregate resin interface reported by some authors [14].

4. Conclusions

These results show that the "pre-treatment" method of application of the silane coupling agent results in greater improvement of the compressive strength of PC than the "integral blend additive" method. The latter method, which is preferable owing to the convenience involved, results in a sufficiently good performance at an optimum level of silane loading (1.0 wt % of resin). Furthermore, of the two silane coupling agents studied, the silane MEMO produced greater improvement of compressive strength than the silane AMEO, under identical conditions of silane loading. Grain size distribution analysis confirms the greater efficiency of the silane MEMO than the silane AMEO, as it showed better adhesion in the case of the former than the latter. X-ray diffraction results show a decrease in peak heights of certain reflections in both sand and PC samples in the presence of the silane coupling agent. These X-ray diffraction results provide indirect evidence for the hypothesis of migration of silane from the resin bulk to the resin–aggregate interface when used as an integral blend additive.

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