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Effect of Mica Surface Treatment on Mechanical Properties of Mica-Flake-Reinforced Cement Composites

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RÉSUMÉ

Pour déterminer comment la modification superficielle du mica influence la résistance à la flexion et la tenue à la rupture de composites à base de ciment renforcé de mica, du mica a été traité par de l'acide fluorhydrique et trois agents copulants : deux silanes (CVBS, γMPS) et un titanate (IDT). On a noté des augmentations significatives des propriétés mécaniques, selon le type de traitement, la concentration de la solution de traitement, le temps de réaction et le rapport eau/ciment.

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EFFECT OF MICA SURFACE TREATMENT ON MECHANICAL PROPERTIES OF MICA-FLAKE-REINFORCED CEMENT COMPOSITES

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ABSTRACT

To determine how the surface modification of mica influences flexural strength and fracture toughness of mica-reinforced cement composites, mica was treated with HF acid and three coupling agents: two silanes (CVBS, γMPS) and a titanate (IDT). Significant increases in mechanical properties resulted, depending on type of treatment, concentration of treating solution, reaction time, and w/c ratio.

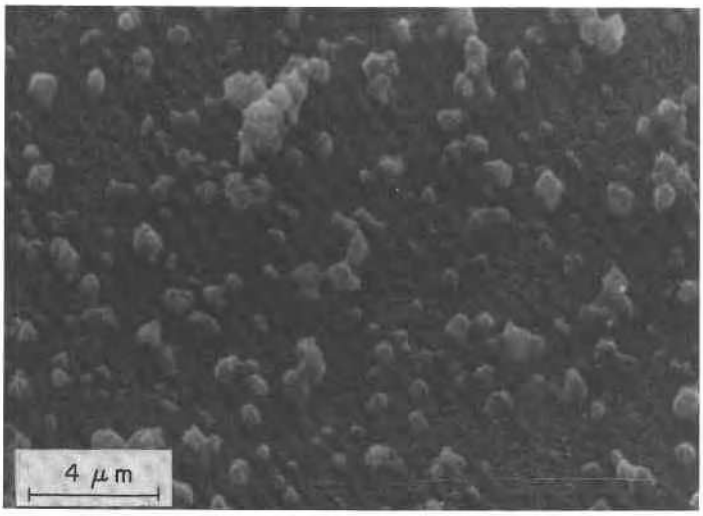
Introduction

In the last decade an increasing number of fibre-reinforced concrete products have become available in which flexural strength and fracture toughness are enhanced by the incorporation of small amounts of fibre reinforcement in the cement matrix (1,2). Numerous inorganic and organic fibres have been marketed, their selection for use as reinforcement depending on engineering properties, cost, chemical stability, and durability in cement matrices. Among them, mica flakes offer a possible low-cost alternative to glass fibres in cement systems (3-6). The addition of mica flakes increases flexural strength and fracture toughness significantly.

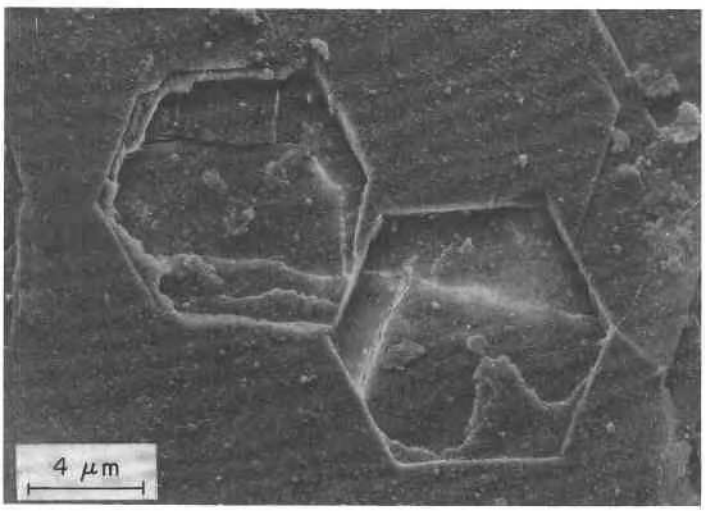
It is generally recognized that the properties of the fibre-matrix interface affect the flexural strength and fracture toughness of cement composite. Equations for predicting flexural strength and fracture toughness contain terms that indicate a direct dependence between these properties and interfacial shear stress (2,7). The objective of the project now reported was to increase the interfacial shear strength in mica flake-reinforced cement composites by chemical modification of the mica surfaces. To achieve this, mica flakes were treated with hydrofluoric acid and three coupling agents (two silanes and a titanate).

Selection of coupling agents was based on work by Favis et al. (8) describing the interaction of silane coupling agents with mica. Their results indicate that the adsorption of individual layers of silane can be controlled down to the first layer and that the selected silane molecules are oriented

normal to the mica surfaces. Plueddemann considers that the preferred orientation of the silane molecules for maximum effectiveness in increasing shear strength would be normal to the surface (9,10), and suggests, as well, that the titanate molecule is oriented normal to the surface.



(a)



(b)

FIG. 1
Surface of a mica flake treated with 24% HF solution for 900 s
(a) typical array of sub-micron protuberances
(b) hexagonal etch pits

Experimental

Materials

Cement: Portland cement composition: C_4AF = 6.7%; C_3A = 12.7%; C_3S = 51.4%; C_2S = 20.3% and $CaSO_4$ = 5.4% as calculated by the Bogue method. Blaine fineness was 300 m^2/kg.

Mica: Phlogopite type, high aspect-ratio reinforcing grade marketed as "Suzorite Mica" (Marietta Resources International Ltd., Montreal, Quebec). Average aspect ratio was approximately 80. The flakes were generally of irregular shape, with a mean width varying between 250 and 1400 μm. Physical and chemical properties of the flakes have been established (6).

Hydrofluoric acid: The acid supplied by Allied Chemical Co. (analysis by Baker and Adamson) was reagent grade HF, 48%.

Coupling agents: Three coupling agents were used: 1) A cationic vinyl benzyl silane (CVBS) (obtained from Dow Corning, Inc.) designated N-β-(N-vinyl benzyl amino) ethyl-γ-aminopropyl trimethoxy silane monohydrogen chloride; 2) a methacrylate functional silane (γMPS) designated γ-methacryloxypropyltrimethoxy silane (obtained from Union Carbide); 3) an isopropyl-tri(dioctylpyrophosphato) titanate (IDT) obtained from Kenrich Petrochemicals, Inc.

A hydrolysis time of 900 s was chosen for the silanes because γMPS is sensitive to the time allotted for hydrolysis and adsorption may be inhibited after longer periods (8).

Mixes: Three sets of cement paste mixes were made, using a conventional Hobart mixer: set 1 comprised control mixes containing no mica; set 2 comprised mixes containing untreated flakes; and set 3 comprised mixes containing treated flakes. Each set was made up of two subsets, one made at w/c = 0.35, the other at w/c = 0.50. In addition, the subsets for set 3 contained four groups of specimens corresponding to the four treatment types. Six test specimens were prepared for each test.

All mica-flake-reinforced cement paste mixes contained 3% by volume of mica; this concentration provides significant increases in strength and toughness of portland cement matrices (5). Samples were demoulded after one day and moist cured for approximately 28 days prior to testing.

Mica Surface Treatment

HF treatment: Preliminary experiments revealed that damage to the flakes was dependent on the ratio of weight of mica to volume of HF. A value of 0.15 was chosen for this ratio. Final selection of the treatment regime for the test program was made after a series of trials, summarized in Table I.

The 24% HF solution with a treatment time of 900 s was used on the mica in the test program (Fig. 1). The mica was washed in water following surface treatment. Energy-dispersive X-ray analysis indicates that treated surfaces, including submicron-size protuberances, are deficient in silica. The Mg/Si ratio was about 3.79 for the treated mica surface and 0.33 for the untreated mica. The protuberances remained attached to the mica surfaces after the washing in the ultrasonic bath. Hexagonal etch pits were also observed (Fig. 1(b)).

Coupling agents: All the experiments with coupling agents involved a solution method. The silane experiments were carried out in aqueous solutions where pH was adjusted to 5.5 with acetic acid; the titanate treatments were carried out in toluene. The silanes were hydrolyzed in deionized water for 900 s, when mica was immediately added to the solution. Adsorption time was determined from the point at which mica was added.

Table I

Treatment of Mica Flakes with HF

Trial	Treatment	Remarks
1.	24% HF, 180 s	Clean surface, no etching
2.	24% HF, 300 s	Clean surface, no etching
3.	24% HF, 600 s	Clean surface, etching starts
4.	24% HF, 900 s	Etched surface, many protuberances
5.	48% HF, 60 s	Etched surface, many protuberances
6.	48% HF, 180 s	Etched surface, protuberances, disintegration starts
7.	48% HF, 300 s	Flakes disintegrating

Suspensions were continuously agitated. All treatments were carried out at a temperature of approximately 23°C. Subsequently, the mica was washed (with distilled water for CVBS, γMPS and toluene for IDT) and filtered with a Büchner funnel. The mica samples were allowed to dry for a short period at 110°C.

Two concentration and three adsorption times for each coupling agent were used. A summary of the treatment schedule is given in Table II.

Table II

Treatment Schedule for Mica-Coupling Agent Mixtures

Coupling Agent	Adsorption Time	Concentration
CVBS	3 000 s 9 000 s 13 000 s	0.5, 1.0 g silane/100 g mica 0.25, 0.50 g silane/L H_2O
γMPS	4 000 s 7 000 s 13 000 s	0.5, 1.0 g silane/100 g mica 0.25, 0.50 g silane/L H_2O
IDT	2 000 s 7 000 s 13 000 s	0.5, 1.0 g titanate/100 g mica 0.25, 0.50 g titanate/L H_2O

Adsorption times were selected to give coverage of one or more molecular layers corresponding to discrete steps or plateaus in the adsorption time curves determined by Favis et al. (8) for the adsorption of these coupling agents on mica surfaces.

Technique

Flexural tests (3-point loading) were carried out using an Instron testing machine and a cross-head speed of 0.100 cm/min. A Cambridge Stereoscan S-250 SEM was used for examining mica surfaces, and a Kevex energy dispersive probe attachment for determining compositional features of mica surfaces.

Results and Discussion

Test results for surface treatments that provided increased composite flexural strength or apparent fracture toughness*, or both, are summarized in Table III; results for treatments with no increases are not included. Flexural strength and apparent toughness values for cement composites containing treated mica are expressed as ratios of corresponding values for composites containing untreated mica. An example is given in Fig. 2 of load-deflection curves used for evaluation of a particular treatment.

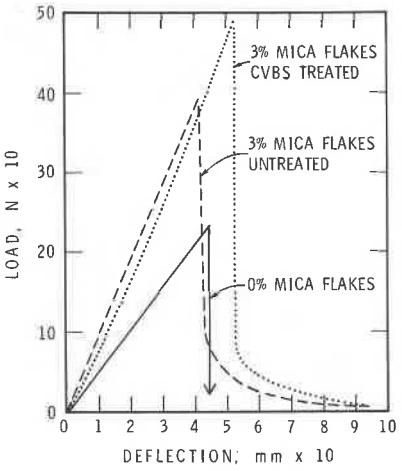


FIG. 2
Load-deflection curves for cement composites containing mica treated with CVBS silane coupling agent, untreated mica, and no mica. Concentration of CVBS = 1%; reaction time = 9000 s

Treatment with 24% HF for 900 s results in a 9% increase in flexural strength and a 29% increase in apparent toughness for w/c = 0.35 specimens. The energy required for pull-out of the mica flakes from the matrix may have increased as a result of greater interfacial friction due to the presence of the etch pits and surface protuberances. The adhesion of the flakes to the matrix was probably not significantly modified, since flexural strength did not increase to any great extent (3). Surface treatment with HF had no beneficial effect on these properties for w/c = 0.50 specimens.

The optimum concentration and reaction time for CVBS-treated mica was 0.5% (weight % of mica) and 3000 s, which is sufficient to provide a monolayer of surface coverage. The increase in apparent fracture toughness was 27%, more than twice the increase in flexural strength. CVBS treatment was not effective for w/c = 0.50.

For γMPS (w/c = 0.35) specimens, a concentration of 0.5% and the lowest reaction time of 4000 s was sufficient to provide a 37% increase in fracture toughness (only 1% less than that for the maximum reaction time). The 4000 s reaction time corresponds to a monolayer of surface coverage (8). At w/c = 0.50 maximum toughness occurred for the longest reaction time, i.e., 13 000 s. Highest flexural strength (w/c = 0.35) was achieved at a concentration of 1% and reaction time of 4000 s, although 0.5% concentration and 13 000 s was almost as effective. The 1%, 4000 s specimens also had the largest increase in toughness. At w/c = 0.50 the maximum observed flexural strength increase was only 10% at 1% γMPS.

For w/c = 0.35 samples, monolayer coverage of γMPS appears to be sufficient to give maximum toughness, whereas maximum strength appears to require more than monolayer coverage. For w/c = 0.50 samples, strength increases were less than 10%, and no clear dependence on concentration and

*Apparent toughness is defined as the work of fracture estimate obtained by integration of the complete load-deflection curve.

Table III

Strength and Toughness Ratios for Cement Composites Containing Treated and Untreated Mica

Treatment	Strength Ratio**	Toughness Ratio	w/c
HF	1.09	1.29	0.35
CVBS			
0.5/3000*	1.12	1.27	0.35
1/3000	1.03	1.19	0.35
1/9000	1.12	1.18	0.35
γMPS			
0.5/4000	1.23	1.37	0.35
1/4000	1.45	1.38	0.35
1/7000	1.05	1.17	0.35
0.5/13 000	1.44	1.31	0.35
1/13 000	1.36	1.21	0.35
0.5/4000	1.08	1.04	0.50
1/4000	1.09	1.19	0.50
0.5/7000	1.00	1.09	0.50
0.5/13 000	1.07	1.38	0.50
1/13 000	1.10	1.28	0.50
IDT			
0.5/2000	-	1.06	0.35
1/2000	-	1.21	0.35
0.5/2000	1.25	1.26	0.50
1/2000	1.05	1.08	0.50
1/7000	1.11	1.33	0.50
0.5/13 000	1.02	1.05	0.50
1/13 000	-	1.30	0.50

*First number refers to the concentration of the coupling agent as a percentage of mica by weight; second number refers to the reaction time in seconds for the coupling agent with mica.

**Strength and toughness ratios are determined by dividing the values of these properties for treated mica systems by values for untreated mica systems. Values are the average for six test specimens.

reaction time was apparent. Maximum toughness requires longer reaction time and multilayer coverage.

For titanate (IDT), the maximum increase in toughness (33%) occurred at intermediate coverage, 1% and 7000 s reaction time (w/c = 0.50). Maximum strength increase (25%) and 26% increase in toughness occurred at 0.5% concentration and 2000 s reaction time. For w/c = 0.35, IDT treatment had no beneficial effect on strength but showed a 21% increase in toughness at 1%, 2000 s reaction time. IDT modification of mica surfaces was more effective for w/c = 0.50 than for w/c = 0.35, in contrast with the results for the two silane treatments.

For HF and silane treatment of mica surfaces, a decrease in the effectiveness of surface modification at higher w/c ratios may be due to fewer contacts between the polymer on the flake surface and the solid matrix because of an increase in total porosity at the interface. This argument does not

Table IV

Effectiveness of Mica Surface Treatment

Flexural Strength	γMPS > CVBS > HF > IDT	
Toughness	γMPS > HF > CVBS > IDT	w/c = 0.35
Flexural Strength	IDT > γMPS	w/c = 0.50
Toughness	γMPS > IDT	

explain, however, why IDT treatment appears to be more effective at higher w/c ratios than at lower ones. Differences in the strengthening mechanism with IDT (compared to silanes) may be related to the larger area occupied by a molecule on the mica surface and the much higher degree of molecular branching (8).

Surface treatments are ranked according to their effectiveness in increasing flexural strength and fracture toughness in Table IV.

Conclusions

1. Flexural strength and fracture toughness of mica-flake-reinforced cement paste can be increased significantly by modification of mica surfaces with HF acid or coupling agents such as silanes and titanates.
2. The effectiveness of HF in treating mica is dependent on the concentration of HF, the volumetric ratio of mica to acid, and the reation time.
3. Increases in flexural strength and toughness are dependent on the concentration of the coupling agent in solution and the reaction of the coupling agent with mica surfaces.
4. Silane coupling agents (CVBS, γMPS) are more effective in increasing strength and toughness of cement composites prepared at a water-cement ratio of 0.35 than at one of 0.50.
5. Monolayer coverage with silane coupling agents apears to be sufficient to provide maximum strength increases for a w/c ratio of 0.35.
6. Multilayer coverage with silane coupling agents is required to provide maximum increases in toughness for a w/c ratio of 0.50.
7. Treatment of mica with a titanate (IDT) is more effective for a w/c ratio of 0.50 than for one of 0.35. Monolayer coverage of mica with IDT provides the best combination of increased flexural strength and fracture toughness.

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