ACI MATERIALS JOURNAL TECHNICAL PAPER

Title no. 97-M39

Cement-Based Materials Improved by Surface-Treated Admixtures

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Cement-based materials containing solid admixtures such as silica fume and short carbon fibers were improved by surface treatment prior to using the admixtures. Consistency, static and dynamic mechanical properties, specific heat, and drying shrinkage were improved. Mortar with high consistency, even without a water-reducing agent, was obtained by using silica fume that had been surface treated with silane. The treatment also increased the strength and modulus, both under tension and compression. In particular, the tensile strength was increased by 31% and the compressive strength was increased by 27%. Moreover, flexural storage modulus (stiffness), loss tangent (damping capacity), and density were increased. The tensile strength of cement paste was increased by 56%, and the modulus and ductility were increased by 39% using silane-treated carbon fibers and silane-treated silica fume, relative to the values for cement paste with as-received carbon fibers and as-received silica fume. Silane treatment of fibers and silica fume contributed approximately equally to the strengthening effect. Silane treatment of fibers and silica fume also decreased the air void content. The effects on strengthening and air void content reduction were less when the fiber treatment involved potassium dichromate instead of silane, and even less when the treatment involved ozone.

The addition of short carbon fibers to cement paste containing silica fume and methylcellulose caused the loss tangent under flexure (≤ 1 Hz) to decrease by up to 25% and the storage modulus (≤ 2 Hz) to increase by up to 67%, such that both effects increased in the following order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers. The addition of methylcellulose to cement paste containing silica fume caused the loss tangent to increase by up to 50% and the storage modulus to decrease by up to 14%. Silane treatment of silica fume had little effect on the loss tangent, but increased the storage modulus by up to 38%. The specific heat of cement paste was increased by 12% and the thermal conductivity was decreased by 40% by using silane-treated silica fume and silane-treated carbon fibers. The specific heat was increased by the carbon fiber addition, due to fiber-matrix interface slippage. The increase was also in the previously described order, due to the increasing contribution of the movement of the fiber-matrix covalent coupling. The specific heat was increased by the silica fume addition, due to slippage at the interface between silica fume and cement. The increase was enhanced by silane treatment of the silica fume. Silane treatment of carbon fibers decreased the thermal conductivity.

Silane treatment of carbon fibers and silica fume increased the effectiveness of these admixtures for reducing the drying shrinkage of cement paste.

Keywords: admixture; cement; concrete; mortar; silica fume; vibration.

INTRODUCTION

Concrete is a cement-based composite made by mixing cement powder, water, aggregates, and optional admixtures such as silica fume and short fibers. The admixtures serve to improve the properties of the resulting concrete. Although the surface treatment of fillers used in polymer-matrix composites is quite common, the surface treatment of fillers used in cement-matrix composites is not. This is partly because of the importance of low cost in practical cement-based material technology. Polymers are much more expensive than cement. Some admixtures used in cement-based materials, however, are much more expensive than cement. As a consequence, the surface treatment of admixtures can be economically feasible and is the subject of this paper.

RESEARCH SIGNIFICANCE

This paper shows that surface treatment of silica fume and short fibers prior to introduction into the cement paste or mortar mixture greatly improves the properties of the resulting cement-based material, relative to the properties of the cement-based material containing admixtures that have not been treated. The improvement includes increased consistency of mixture (for ease of placement), decreased drying shrinkage (reduced tendency for cracking during shrinkage), increased strength and modulus of concrete (for structural integrity), decreased content of air voids (for structural integrity), increased specific heat (for heat retention), and decreased thermal conductivity (for thermal insulation). A particularly effective surface treatment involves coating the admixture with a hydrophylic material such as silane.

A.—IMPROVING CONSISTENCY AND STRENGTH OF SILICA FUME MORTAR BY USING SILANE-TREATED SILICA FUME

The addition of silica fume to concrete is effective for increasing the compressive strength,[1-4] decreasing the drying shrinkage,[3,4] increasing the abrasion resistance,[5] increasing the bond strength with the reinforcing steel,[6,7] and decreasing the permeability.[8] As a result, silica fume concrete is increasingly used in civil structures.[9,10] Silica fume causes a decrease in workability, however, which is a barrier against proper utilization of silica fume concrete.[11] In this section, it is reported that the consistency (slump) of silica fume mortar can be greatly enhanced by using silane treated silica fume, that is, silica fume that has been coated by a silane coupling agent prior to incorporation in the mixture.

It has been recently reported[12] that the surface treatment of silica fume with sulfuric acid prior to incorporation in a cement matrix results in mortars exhibiting increases in tensile strength by 12% and compressive strength by 14%, relative to the values obtained by using as-received silica fume. In this paper, it is reported that a different surface treatment that involves the use of a silane coupling agent provides increases in tensile strength of 31% and compressive strength of 27%, thus resulting in high-strength mortar with a tensile strength of 3.1 MPa and a compressive strength of 78 MPa.

ACI Materials Journal, V. 97, No. 3, May-June 2000.

MS No. 99-106 received September 20, 1999, and reviewed under Institute publication policies. Pertinent discussion will be published in the March-April 2001 *ACI Materials Journal* if received by December 1, 2000.

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The use of silane coupling agents is common for enhancing the bond between a ceramic filler and a polymer matrix[13] because the epoxy structure at the end of the silane molecule allows coupling to an epoxy matrix. However, silane coupling agents have not been previously used for enhancing the bond between a ceramic filler and a cement matrix. In spite of the difference in chemical structure between cement and polymers, it was found that silane coupling agents are effective for both types of matrixes. The effectiveness of silane for cement is due to the reactivity of its molecular ends with -OH groups and the presence of -OH groups on the surface of both silica and cement. Moreover, the hydrophylic nature of silane is expected to improve the workability of the mixture and to enhance the dispersion of admixtures in the mixture.

Experimental methods and materials

The cement used was portland cement (Type I). The silica fume was used in the amount of 15% by weight of cement. This amount of silica fume was chosen because it is commonly used in carbon fiber-reinforced cement, in which silica fume helps the fiber dispersion. The combined use of silica fume and carbon fibers will be addressed in an upcomming section. The silane coupling agent used was a 1:1 (by weight) mixture of $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$ (referred to as S_1) and $OCH_2CHCH_2OCH_2CH_2CH_2Si(OCH_3)_3$ (referred to as S_2). The amine group in S_1 serves as a catalyst for the curing of epoxy and consequently allows the S_1 molecule to attach to the epoxy end of the S_2 molecule. The trimethylsiloxy ends of the S_1 and S_2 molecules then connect to the -OH functional group on the surface of silica fume The silane was dissolved in ethylacetate. Surface treatment of silica fume was performed by immersing the silica fume in the silane solution, heating to 75 C while stirring, and holding at 75 C for 1 h, followed by filtration, washing with ethylacetate, and drying. After this, the silica fume was heated in a furnace at 110 C for 12 h.

The fine aggregate used for mortars was natural sand (all passing No. 4 U. S. sieve, 99.9% SiO_2). The particle size analysis of the sand is shown in Fig. 1 of Reference 14. No coarse aggregate was used, and the sand/cement ratio was 1.0. The water-cement ratio (w/c) was 0.35. A water-reducing agent (sodium salt of a condensed naphthalenesulphonic acid) was used in the amount of 1% of cement weight for mortars with as-received silica fume and 0.2% of cement weight for mortars with treated silica fume, unless stated otherwise. Because the silane treatment greatly enhanced the workability, the need for a water reducing agent was significantly decreased by the treatment. In fact, a water reducing agent was not needed at all when silane treated silica fume was used (Table 1). All ingredients were mixed in a rotary mixer with a flat beater by: 1) mixing the solid components at a very low speed for 2 min; 2) adding the liquid components and mixing at a low speed for 2 to 3 min; and 3) mixing at a high speed for 7 to 8 min. After placing the mortar into the molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured at room temperature with a relative humidity of 100% for 28 days. The consistency of the mortar mixtures was tested by measuring the slump in accordance with the ASTM C 143-90a method.

For compressive testing according to ASTM C 109-80, specimens were prepared by using a 2 x 2 x 2 in. (5.1 x 5.1 x 5.1 cm) mold. Compression testing was performed using a hydraulic material testing system. The cross-head speed was 1.27 mm/min. Dog-bone shaped specimens of the dimensions shown in Fig. 1 of Reference 15 were used for tensile testing. They were prepared by using molds of the same shape and size. Tensile testing was performed using a screw-type mechanical testing system. The displacement rate was 1.27 mm/min. During loading, the strain was measured by the cross-head displacement in compressive testing and with a strain gage in tensile testing. Six specimens of each composition were tested.

Dynamic mechanical testing (ASTM D 4065-94) at controlled frequencies (0.2, 1.0, and 2.0 Hz) and room temperatures (20 C) were conducted under flexure using a dynamic mechanical analyzer. Measurements of tan δ (damping capacity, equal to the ratio of the loss modulus to the storage modulus, that is, the ratio of the imaginary part of the complex modulus to the real part of the complex modulus) and storage modulus (stiffness, that is, the real part of the complex modulus) were made simultaneously as a function of temperature at various constant frequencies. The heating rate was 2 C/min, which was selected to prevent any artificial damping peaks that may be caused by higher heating rates. The specimens were in the form of beams (120 x 8 x 3 mm) under three-point bending, with a span of 115 mm. The loads used were all large enough that the amplitude of the specimen deflection ranged from 6.5 to 9 μm (which is over the minimum value of 5 μm required by the equipment for accurate results). The loads were set so that each different type of specimen was always tested at its appropriate stress level. Six specimens of each type were tested.

Results

Table 1 shows that the silane treatment caused the silica fume mortar mixture to increase in slump. With silane-treated silica fume and no water-reducing agent, the slump was larger than that of the mixture with as-received silica fume and water-reducing agent in the amount of 1% by weight of cement. With silane-treated silica fume and water-reducing agent in the amount of 0.2% by weight of cement, the slump was similar to that of the mixture with as-received silica fume and water-reducing agent in the amount of 2% by weight of cement.

Table 2 shows that the tensile strength, tensile modulus, compressive strength, and compressive modulus of silane-treated silica fume mortar increased significantly when compared with mixtures without treatment. In addition, the tensile and compressive ductilities increased slightly. The density was also increased by the treatment. Table 3 shows that the storage modulus, loss modulus, and loss tangent of silane-treated silica fume mortar increase substantially when compared with mixtures without treatment.

Discussion

The increase in consistency (slump) due to silane treatment was due to the improved wetability of silica fume by water after the silane treatment. The improved wetability was expected from the hydrophylic nature of the silane molecule. The improved wetability may result in improved dispersion of the silica fume.

The science behind sulfuric acid treatment[12] and silane treatment of silica fume is different. Sulfuric acid treatment roughens the surface of silica fume, as shown by specific surface area measurement[12]. This is a result of the chemical attack on the silica fume by the acid. Silane treatment involves formation of a silane coating on the surface of the silica fume, however, which does not cause surface roughening. The ability of silane treatment to improve the bond between silica fume and cement

Table 1—Slump of mortar mixture

Silica fume	Water-reducing agent/cement, %	Slump, mm
As received	0	150
As received	1	186
As received	2	220
Silane treated	0	194
Silane treated	0.2	215

Table 2—Tensile and comprehensive properties, and density of mortars with silica fume (with and without silane treatment)

	Without treatment	With treatment
Tensile strength, MPa	2.35 ± 0.11	3.09 ± 0.13
Tensile modulus, GPa	10.2 ± 0.07	14.57 ± 0.08
Tensile ductility, %	0.0141 ± 0.0003	0.0150 ± 0.0004
Compressive strength, MPa	61.95 ± 2.3	78.4 ± 3.2
Compressive modulus, GPa	21.08 ± 0.54	28.7 ± 0.46
Compressive ductility, %	0.138 ± 0.002	0.145 ± 0.003
Density, g/cm^3 *	2.13	2.20

*Measured by using water and Archimedes' Principle.

Table 3—Dynamic flexual properties of mortars with silica fume (with and without treatment)

	Without treatment	With treatment
Storage modulus, GPa		
0.2 Hz	20.30 ± 0.02	31.8 ± 0.02
1.0 Hz	20.05 ± 0.02	31.5 ± 0.03
2.0 Hz	19.88 ± 0.02	31.1 ± 0.03
Loss modulus, GPa*		
0.2 Hz	0.24 ± 0.02	0.74 ± 0.02
1.0 Hz	3×10^{-4}	5×10^{-4}
2.0 Hz	2×10^{-4}	5×10^{-4}
Loss tangent		
0.2 Hz	0.0120	0.0234
1.0 Hz	1×10^{-5}	2×10^{-5}
2.0 Hz	1×10^{-5}	2×10^{-5}

* Product of storage modulus and loss tangent.

matrix (as shown by the improvement in tensile and compressive properties, Table 2) is associated with the chemical coupling provided by the silane between silica fume and cement. The coupling results in an increase in density (Table 2), which contributes to the increases in tensile and compressive strengths. The increase in storage modulus (Table 3) is consistent with the increases in tensile and compressive moduli (Table 2). The increase in loss tangent (Table 3) is probably due to the contribution of the silane coating to viscoelastic damping.

Compared to the sulfuric acid treatment, silane treatment is less hazardous and is of less concern to the pH of the concrete. The pH of concrete affects the corrosion resistance of steel reinforcement in concrete.

B.—CARBON FIBER-REINFORCED CEMENT IMPROVED BY USING SILANE-TREATED CARBON FIBERS

Cement reinforced with short carbon fibers is attractive due to its high flexural strength and toughness and low drying shrinkage, in addition to its strain sensing ability.[5,16-26] Surface treatment of carbon fibers by ozone has been shown to be effective for improving the wetability by water, thereby improving the fiber-matrix bond; increasing the tensile strength, modulus, and ductility beyond the levels attained with untreated carbon fibers, and decreasing the drying shrinkage below the levels attained with untreated fibers.[27] It was reported in Section A that the surface treatment of silica fume by using a silane coupling agent increases the consistency and improves the strengths (tensile and compressive) of cement mortar beyond the levels attained by using untreated silica fume. That the silane treatment conducted on carbon fibers improves the mechanical properties of carbon fiber-reinforced cement paste beyond the levels attained by using ozone treated carbon fibers will now be discussed.

Silica fume is commonly used along with carbon fibers to help the dispersion of the fibers in the cement mixture.[20] It will also be reported herein that the combined use of silane treated carbon fibers and silane treated silica fume results in mechanical properties that are superior to those attained by silane treated carbon fibers in combination with untreated silica fume or those attained by untreated carbon fibers in combination with silane treated silica fume.

Experimental methods and materials

The carbon fibers were isotropic pitch based, unsized, and approximately 5 mm in length. The fiber properties are shown in Table 4. As-received and three types of surface treated fibers were used. The fiber content was 0.5% by weight of cement. The fiber surface treatments involved: 1) ozone (O_3); 2) an

Table 4—Properties of carbon fibers

Filament diameter	15 ± 3 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	3.0×10^{-3} Ω.cm
Specific gravity	1.6 g cm^{-3}
Carbon content	98 wt.%

aqueous solution of potassium dichromate ($K_2Cr_2O_7$, 30 wt.%) and sulfuric acid (H_2SO_4, 40 wt.%, which enhances the oxidation ability); and 3) silane. The ozone treatment for surface oxidation involved exposure of the fibers to O_3 gas (0.6 vol %, in O_2) at 160 C for 5 min. Prior to O_3 exposure, the fibers had been dried at 160 C in air for 30 min. The potassium dichromate treatment for surface oxidation involved immersing in the dichromate solution and heating to 60 C while stirring for 2 h, followed by filtration and washing with water, and then drying at 110 C for 6 h. For the silane treatment, the silane coupling agent was a 1:1 (by weight) mixture of S_1 and S_2, as described in Section A. The trimethylsiloxy ends of the S_1 and S_2 molecules connect to the -OH functional group on the surface of silica fume or carbon fibers. The procedure of silane treatment was the same as that in Section A.

No aggregate (fine or coarse) was used. The *w/c* was 0.35. A water-reducing agent (the same as in Section A) was used in the amount of 2% by weight of cement.

The cement and silica fume (15% by weight of cement) were as described in Section A. Methylcellulose was used in the amount of 0.4% by weight of cement. A defoamer, used whenever methylcellulose was used, was in the amount of 0.13 vol %. Silica fume and methylcellulose were used along with carbon fibers to help the dispersion of the fibers in the cement mixture.[20] Mixing was conducted as in Section A. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for approximately 2 min. Then this mixture (if applicable), cement, water, water-reducing agent, silica fume, and fibers (if applicable) were mixed in the mixer for 10 min. After placing into molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured as described in Section A.

Tensile testing was performed as in Section A. The strain was measured by using a resistive strain gage that was mounted on each specimen. Four specimens of each composition were tested. Twelve compositions, as listed in Table 5, were studied. Six of the compositions had as-received silica fume; the other six had silane-treated silica fume.

The air void content was measured by using ASTM method C185-95. Three specimens of each composition were tested.

Results

Table 5 and 6 show the tensile strength and modulus, respectively, of 12 types of cement pastes. The strength is slightly increased by the addition of methylcellulose and defoamer, but the modulus is slightly decreased by the addition of methylcellulose and defoamer. Both strength and modulus, however, are increased by the addition of fibers. The effectiveness of the fibers in increasing strength and modulus increases in the following order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives substantially higher strength and modulus than as-received silica fume. The highest tensile strength and modulus are exhibited by cement paste with silane-treated silica fume and silane-treated fibers. The strength is 56% higher and the modulus is 39% higher than those of the cement paste with as-received silica fume and as-received fibers. The strength is 26% higher and the modulus is 14% higher than those of the cement paste with as-received silica fume and silane-treated fibers. Hence, silane treatments of silica fume and fibers are approximately equally valuable in providing strengthening.

Table 7 shows the tensile ductility. It is slightly increased by the addition of methylcellulose and defoamer, and is further increased by the further addition of fibers. The effectiveness of the fibers in increasing the ductility also increases in the previously described order. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations involving surface treated fibers, silane-treated silica fume gives higher ductility than as-received silica fume. The highest ductility is exhibited by cement paste with silane-treated silica fume and silane-treated fibers. The ductility is 39% higher than that of the cement paste with as-received silica fume and as-received fibers. It is 14% higher than that of the cement paste with as-received silica fume and silane-treated fibers.

Table 8 shows the air void content. It is decreased by the addition of methylcellulose and defoamer, but is increased by the further addition of fibers, whether or not the fibers have been surface treated. Among the formulation with fibers, the air void content decreases in the following order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations (including those without fibers), silane-treated silica fume gives lower air void content than as-received silica fume.

Discussion

The hydrophylic nature of the silane molecule is believed to improve the bond between fiber and cement paste, or between silica fume and cement paste, thereby increasing the tensile strength, modulus, and ductility, and decreasing the air void content of the cement-matrix composite. Both ozone treatment and dichromate treatment involve surface oxidation; the oxidation results in oxygen-containing functional groups that help improve the hydrophylicity. The dichromate treatment is more effective than the ozone treatment (probably due to the greater uniformity of the resulting surface treatment), but both ozone and dichromate treatments are inferior to the silane treatment. Silane treatment has not been previously used for carbon fibers for use in cement. The superiority of the silane treatment over the other two treatments of the fibers applies whether the silica fume is as-received or silane-treated.

The ozone treatment is the most expensive of the three treatments, due to the high temperature and gas handling. The silane treatment is more expensive than the dichromate treatment, due to the need to recycle the solvent, ethylacetate.

C.—EFFECT OF CARBON FIBERS AND SURFACE TREATMENTS ON VIBRATION REDUCTION ABILITY OF CEMENT

Reducing the vibrations in concrete structures is valuable for hazard mitigation and structural control. Admixtures such as silica fume, latex, and methylcellulose are known to improve the vibration reduction ability of cement paste through increases in both loss tangent and storage modulus, as measured under dynamic flexure.[28] The addition of sand is known to degrade the vibration reduction ability of cement paste through decreases in both loss tangent and storage modulus.[29] The positive effect of silica fume on the loss tangent is due to the small particle size of silica fume and the resulting large area of the interface between silica fume and cement. The positive effect of latex and methylcellulose on the loss tangent is due to the viscoelastic damping by these polymers. The negative effect

Table 5—Tensile strength, MPa, of cement pastes with and without fibers

Formulation	As-received silica fume	Silane-treated silica fume
A	1.53 ± 0.06	2.04 ± 0.06
A^+	1.66 ± 0.07	2.25 ± 0.09
A^+F	2.00 ± 0.09	2.50 ± 0.11
A^+O	2.25 ± 0.07	2.67 ± 0.09
A^+K	2.32 ± 0.08	2.85 ± 0.11
A^+S	2.47 ± 0.11	2.50 ± 0.11

A: cement + water + water reducing agent + silica fume.
A^+: A^+ methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

Table 6—Tensile modulus, GPa, of cement pastes with and without fibers

Formulation	As-received silica fume	Silane-treated silica fume
A	10.2 ± 0.7	11.5 ± 0.6
A^+	9.3 ± 0.5	10.7 ± 0.4
A^+F	10.9 ± 0.3	12.9 ± 0.7
A^+O	11.9 ± 0.3	13.1 ± 0.6
A^+K	12.7 ± 0.4	14.3 ± 0.4
A^+S	13.3 ± 0.5	15.2 ± 0.8

A: cement + water + water reducing agent + silica fume.
A^+: A^+ methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

Table 7—Tensile ductility, %, of cement pastes with and without fibers

Formulation	As-received silica fume	Silane-treated silica fume
A	0.020 ± 0.0004	0.020 ± 0.0004
A^+	0.023 ± 0.0004	0.021 ± 0.0004
A^+F	0.025 ± 0.0003	0.024 ± 0.0004
A^+O	0.026 ± 0.0003	0.027 ± 0.0004
A^+K	0.028 ± 0.0003	0.030 ± 0.0004
A^+S	0.031 ± 0.0004	0.034 ± 0.0004

A: cement + water + water reducing agent + silica fume.
A^+: A^+ methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

Table 8—Air void content (%, ± 0.12) of cement pastes with and without fibers

Formulation	As-received silica fume	Silane-treated silica fume
A	3.73	3.26
A^+	3.42	3.01
A^+F	5.32	4.89
A^+O	5.07	4.65
A^+K	5.01	4.49
A^+S	4.85	4.16

A: cement + water + water reducing agent + silica fume.
A^+: A^+ methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

of sand on the loss tangent is due to the large particle size of sand (compared to that of silica fume) and the greater degree of compositional homogeneity within a sand particle than that within cement paste; in other words, the volume occupied by sand is less effective for damping than the volume occupied by cement paste.

Short fibers are used as an admixture to decrease the drying shrinkage and increase the flexural toughness. In the case of carbon fibers, the flexural strength is also enhanced.[16,17,23-26] They are typically used along with silica fume, which helps the fiber dispersion in the mixture.[20] The effect of fiber addition on the vibration reduction ability has not been previously reported. This paper is focused on this effect for the case of carbon fibers. Included in the study is the effect of fiber surface treatment, which enhances the bond between fiber and cement matrix, thereby increasing the tensile strength, modulus, and ductility of the composite.[15,30]

Experimental methods and materials

Material sources and preparation methods are as described in Section B. Dynamic mechanical testing was performed as in Section A. Three specimens of each composition were tested. Twelve compositions, as listed in Table 2, were studied.

Results

Tables 9 to 11 give the dynamic flexural properties of 12 types of cement pastes. Six of the types have as-received silica fume; the other six have silane-treated silica fume.

The loss tangent (Table 9) is increased slightly by the addition of methylcellulose. Further addition of carbon fibers decreases the loss tangent. The loss tangent decreases in the following order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers, at least for the case of as-received silica fume at 0.2 Hz.

The storage modulus (Table 10) is decreased by the addition of methylcellulose. Further addition of carbon fibers increases the storage modulus, such that the modulus increases in the order: as-received fibers, ozone-treated fibers, dichromate-treated fibers and silane-treated fibers. These trends apply whether the silica fume is as-received or silane-treated, and whether the frequency is 0.2, 1.0, or 2.0 Hz.

The loss modulus (Table 11, product of loss tangent and storage modulus) is increased by the addition of methylcellulose, except for the case of the paste with silane-treated silica fume at 0.2 Hz. Further addition of carbon fibers increases the loss modulus very slightly, if at all.

Discussion

Carbon fibers are effective for increasing the storage modulus, particularly if they are surface treated. However, they decrease the loss tangent, particularly if they are surface treated. The increase in storage modulus is due to the reinforcing ability of the fibers. The decrease in loss tangent is probably similar in origin to the decrease in loss tangent upon the addition of sand,[29] that is, the fiber diameter (15 μm) is not small enough for the fiber-matrix interface area to be large enough for enhancing damping significantly. The stronger the fiber-matrix interface, as indicated by an increase in storage modulus, the lower the loss tangent. This is due to the decrease in the ability of the fiber-matrix interface to contribute to damping when the interface is stronger. The tensile strength depends on the fiber surface treatment[31] in exactly the same way as the storage modulus, that is, the higher the strength, the higher the modulus.

For vibration reduction, a high loss tangent and a high storage modulus are desirable. The loss modulus is a figure of merit that combines both virtues. Due to the opposite trends of loss tangent and storage modulus upon fiber addition or methylcellulose addition, the loss modulus is insignificantly changed by fiber or methylcellulose addition. Thus, carbon fiber addition is not effective for enhancing the ability of cement paste containing silica fume to reduce vibrations.

The addition of methylcellulose to cement paste containing silica fume (but no fiber) causes the loss tangent to increase by up to 50% and the storage modulus to decrease by up to 14%, as expected from the viscoelastic nature of methylcellulose and the high stiffness of cement paste with silica fume. In contrast, the addition of methylcellulose to plain cement paste (without silica fume) causes both loss tangent and storage modulus to increase.[28]

Comparison of cement pastes with as-received and silane-treated silica fume shows that silane treatment of silica fume has little effect on the loss tangent, but increases the storage modulus by up to 38%. The increase in storage modulus is believed to be due to the strengthening of the interface between silica fume and cement. Consistent with the increase in storage modulus is the increase in tensile strength (Section B).

D.—INCREASING SPECIFIC HEAT OF CEMENT PASTE BY ADMIXTURE SURFACE TREATMENT

The specific heat of a material is the amount of heat required to heat up 1 g of the material by 1 C. A high specific heat means high ability for retaining heat—an ability that is desirable for energy conservation in buildings. It has been previously reported that admixtures (that is, silica fume, latex, methylcellulose, or carbon fibers) increase the specific heat of cement paste.[30] For example, the addition of silica fume in the amount of 15% by weight of cement increases the specific heat by 9%; the addition of methylcellulose in the amount of 0.4% by weight of cement increases the specific heat by 4%.[30] The surface treatment of admixtures such as silica fume[12] (Sections A, B, and C) and carbon fibers (Sections B and C) has been reported to improve the mechanical properties, decrease the air void content, and improve the workability of cement paste. A particularly effective surface treatment involves the use of a silane coupling agent. As the effect of surface treating an admixture on the specific heat has not been previously

Table 9—Loss tangent (tan δ, ± 0.002) of cement pastes

	With as-received silica fume			With silane-treated silica fume		
Formulation	0.2 Hz	1.0 Hz	2.0 Hz	0.2 Hz	1.0 Hz	2.0 Hz
A	0.082	0.030	$< 10^{-4}$	0.087	0.032	$< 10^{-4}$
A^+	0.102	0.045	$< 10^{-4}$	0.093	0.040	$< 10^{-4}$
A^+F	0.089	0.033	$< 10^{-4}$	0.084	0.034	$< 10^{-4}$
A^+O	0.085	0.043	$< 10^{-4}$	0.084	0.032	$< 10^{-4}$
A^+K	0.079	0.039	$< 10^{-4}$	0.086	0.035	$< 10^{-4}$
A^+S	0.076	0.036	$< 10^{-4}$	0.083	0.033	$< 10^{-4}$

A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

Table 10— Storage modulus (GPa, ± 0.03) of cement pastes

Formulation	With as-received silica fume			With silane-treated silica fume		
	0.2 Hz	1.0 Hz	2.0 Hz	0.2 Hz	1.0 Hz	2.0 Hz
A	12.71	12.14	11.93	16.75	16.21	15.95
A^+	11.52	10.61	10.27	15.11	14.73	14.24
A^+F	13.26	13.75	13.83	17.44	17.92	18.23
A^+O	14.14	14.46	14.72	18.92	19.36	19.57
A^+K	15.42	16.15	16.53	19.33	19.85	20.23
A^+S	17.24	17.67	15.95	21.34	21.65	21.97

A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

Table 11—Loss modulus (GPa, ± 0.03) of cement pastes

	With as-received silica fume			With silane-treated silica fume		
Formulation	0.2 Hz	1.0 Hz	2.0 Hz	0.2 Hz	1.0 Hz	2.0 Hz
A	1.04	0.39	$< 10^{-3}$	1.46	0.52	$< 10^{-3}$
A^+	1.18	0.48	$< 10^{-3}$	1.41	0.59	$< 10^{-3}$
A^+F	1.18	0.45	$< 10^{-3}$	1.47	0.61	$< 10^{-3}$
A^+O	1.20	0.62	$< 10^{-3}$	1.59	0.62	$< 10^{-3}$
A^+K	1.22	0.63	$< 10^{-3}$	1.66	0.70	$< 10^{-3}$
A^+S	1.31	0.63	$< 10^{-3}$	1.77	0.71	$< 10^{-3}$

A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A^+ + silane-treated fibers.

investigated, this section is aimed at studying this effect. It was found that admixture surface treatment increases the specific heat of cement paste.

In addition to a high specific heat, a low thermal conductivity is desired for the purpose of thermal insulation of buildings. It has been reported that admixtures (that is, silica fume, latex, or methylcellulose) decrease the thermal diffusivity, thereby decreasing the thermal conductivity.[30] It has also been reported that the addition of carbon fibers in the amount of 0.5% by weight of cement increases the thermal diffusivity, thereby increasing the thermal conductivity.[30] The secondary objective of this section is to investigate the effect of admixture surface treatment on the thermal conductivity of cement paste. The admixtures investigated in this work are silica fume, methylcellulose (used together with a defoamer), and short carbon fibers.

Experimental methods and materials

Material sources and preparation methods are as described in Section B.

The thermal conductivity (in W/mK) was given by the product of the thermal diffusivity (in cm^2/s), specific heat (in J/gK) and density (in g/cm^3). For measuring the thermal diffusivity, the laser flash method was used. In this method, a pulsed laser and a computer with a data acquisition board were used. The specimen was in the form of a disc with a 13 mm diameter and a 2 mm thickness. Sample preparation for laser diffusivity measurement involved: 1) polishing both sides of the sample; 2) coating both sides of the sample with gold for thermal contacts; and 3) coating one of the sides (the side on which the laser beam would hit) with carbon (for avoiding reflection of the laser beam, since carbon is black). The temperature of the specimen at the side without carbon coating was measured after the laser flash as a function of time by using a thermocouple. From the temperature-versus-time curve, the thermal diffusivity was calculated. Six specimens of each type were tested.

A differential scanning calorimeter (DSC) was used for measuring the specific heat. A three-curve analysis method was used that involved obtaining a DSC sample, baseline, and reference material data. Sapphire was selected as a reference material. The specimen was in the form of a disc 6 mm in diameter and 1 mm in thickness. Six specimens of each type were tested.

The density was measured by weight and volume (dimensions) measurements. Six specimens of each type were tested.

Twelve compositions, as listed in Table 12, were studied. Six of the compositions had as-received silica fume; the other six had silane-treated silica fume. In addition to these 12 compositions, plain cement paste (with cement and water only, $w/c = 0.45$) was studied for the sake of comparison.

Results

Table 12 shows the specific heat of cement pastes. The specific heat is significantly increased by the addition of silica fume, as previously reported.[30] It is further increased by the further addition of methylcellulose and defoamer. It is still further increased by the still further addition of carbon fibers. The effectiveness of the fibers in increasing the specific heat increases in the following order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives higher specific heat than as-received silica fume. The highest specific heat is exhibited by the cement paste with silane-treated silica fume and silane-treated fibers. The specific heat is 12% higher than that of plain cement paste, 5% higher than that of the cement paste with as-received silica fume and as-received fibers, and 0.5% higher than that of the cement paste with as-received silica fume and silane-treated fibers. Hence, silane treatment of fibers is more valuable than that of silica fume for increasing the specific heat.

Table 13 shows the thermal diffusivity of cement pastes. The thermal diffusivity is significantly decreased by the addition of silica fume, as previously reported.[30] The further addition of methylcellulose and defoamer, or the still further addition of fibers has relatively little effect on the thermal diffusivity. Surface treatment of the fibers by ozone or dichromate slightly increases the thermal diffusivity, whereas surface treatment of the fibers by silane slightly decreases the thermal diffusivity. These trends apply whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly lower (or essentially the same) thermal diffusivity than as-received silica fume. Silane treatments of silica fume and of fibers are approximately equally effective for lowering the thermal diffusivity.

Table 14 shows the density of cement pastes. The density is significantly decreased by the addition of silica fume, as previously reported.[30] It is further decreased slightly by the further addition of methylcellulose and defoamer. It is still further decreased by the still further addition of fibers. The effectiveness of the fibers in decreasing the density decreases in the following order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly higher (or essentially the same) specific heat than as-received silica fume. Silane treatment of fibers is more valuable than that of silica fume for increasing the density.

Table 15 shows the thermal conductivity. It is significantly decreased by the addition of silica fume, as previously reported.[30] The further addition of methylcellulose and defoamer or the still further addition of fibers has little effect on the density. Surface treatment of the fibers by ozone or dichromate slightly increases the thermal conductivity, whereas surface treatment of the fibers by silane has negligible effect. These trends apply whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly lower (or essentially the same) thermal conductivity as as-received silica fume. Silane treatments of silica fume and of fibers contribute comparably to reducing the thermal conductivity.

Discussion

As explained in Reference 30: 1) silica fume increases the specific heat of cement paste because of the interface (however diffuse) between silica fume and cement, and the contribution of interfaces to the component of specific heat associated with vibrations; 2) methylcellulose increases the specific heat of cement paste because of the molecular nature of methylcellulose and the contribution of molecular movements to the specific heat; and 3) fibers increase the specific heat of cement paste because of the interface between fibers and the cement matrix. In this work, it was found that silane treatment of silica fume or fibers increases the specific heat. This is due to the contribution of the movement of the covalent coupling between silica fume and cement matrix, and between fiber and cement matrix. Surface treatment of fibers by ozone or dichromate also increases the specific heat (though the increase is not as much as that for silane treatment), due to the surface oxidation, the resulting active functional groups on the fiber surface and the consequent fiber-matrix covalent coupling, the movement of which contributes to the specific heat. These explanations are supported by the following argument.

Correlation with the results on the effect of fiber surface condition on the loss tangent under dynamic flexural testing (Section C) shows that a higher specific heat is associated with

Table 12—Specific heat (J/gK, ± 0.001) of cement pastes

Formulation	As-received silica fume	Silane-treated silica fume
A	0.782	0.788
A^+	0.793	0.803
A^+F	0.804	0.807
A^+O	0.809	0.813
A^+K	0.812	0.816
A^+S	0.819	0.823

Value for plain cement paste (with cement and water only) is 0.736 J/gK.
A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A+ + silane-treated fibers.

Table 13—Thermal diffusivity (mm^2/s, ± 0.03) of cement pastes

Formulation	As-received silica fume	Silane-treated silica fume
A	0.26	0.24
A^+	0.25	0.22
A^+F	0.27	0.26
A^+O	0.29	0.27
A^+K	0.29	0.27
A^+S	0.25	0.23

Value for plain cement paste (with cement and water only) is 0.736 J/gK.
A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A+ + silane-treated fibers.

Table 14—Density (g/cm^3, ± 0.02) of cement pastes

Formulation	As-received silica fume	Silane-treated silica fume
A	1.72	1.73
A^+	1.69	1.70
A^+F	1.62	1.64
A^+O	1.64	1.65
A^+K	1.65	1.66
A^+S	1.66	1.68

Value for plain cement paste (with cement and water only) is 0.736 J/gK.
A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A+ + silane-treated fibers.

Table 15—Thermal conductivity (W/mK, ± 0.03) of cement pastes

Formulation	As-received silica fume	Silane-treated silica fume
A	0.35	0.33
A^+	0.34	0.30
A^+F	0.35	0.34
A^+O	0.38	0.36
A^+K	0.39	0.37
A^+S	0.34	0.32

Value for plain cement paste (with cement and water only) is 0.736 J/gK.
A: cement + water + water-reducing agent + silica fume.
A^+: A + methycellulose + defoamer.
A^+ F: A^+ + as-received fibers.
A^+ O: A^+ + O_3-treated fibers.
A^+ K: A^+ + dichromate-treated fibers.
A^+ S: A+ + silane-treated fibers.

a lower loss tangent. A lower loss tangent is associated with less fiber-matrix interface slippage (the main mechanism of vibration damping in a fiber composite without a viscoelastic component), which in turn is associated with less contribution of the interface to the component of specific heat due to vibrations. Thus, the effect of fiber surface condition on the specific heat (Table 12) cannot be explained in terms of the fiber-matrix interface slippage. Rather, it is explained in terms of the movement of the covalent coupling between fiber and matrix.

Correlation with the results on the effect of silica fume surface condition on the loss tangent of cement paste with silane-treated or dichromate-treated carbon fibers (Section C) shows that a higher specific heat is associated with a higher loss tangent at 0.2 Hz. Thus, the increase of specific heat due to the silane treatment of silica fume is probably related to enhanced slippage at the interface (however diffuse) between silica fume and cement. The movement of the silane molecules, however, probably also contributes to this. As mentioned in the Results subsection of this section, the effect of silane treatment of silica fume on the specific heat is small compared to that of silane treatment of carbon fibers on the specific heat.

Silica fume decreases the thermal diffusivity of cement paste, partly because of the interface (however diffuse) between silica fume and cement, the contribution of the interface to the thermal resistance, and partly because of the low thermal diffusivity of silica fume. The addition of methylcellulose and defoamer slightly decreases the thermal diffusivity because of the low thermal conductivity of molecular materials. Silane treatment of silica fume or fibers slightly decreases the thermal diffusivity, due to the molecular nature of silane. Ozone and dichromate treatments of fibers slightly increase the thermal diffusivity (due to the surface oxidation and the resulting fiber-matrix covalent coupling), which probably strengthens the fiber-matrix interface[27] and probably decreases the thermal resistance of the interface. Another reason may be that the treatments enhance the wetability of fibers, thereby increasing the degree of fiber dispersion and decreasing the porosity.

Silica fume decreases the density of cement paste (Table 14) because of the increase in air void content (Table 8). The addition of methylcellulose and defoamer decreases the density slightly, in spite of the decrease in air void content. This is attributed to the low density of these molecular materials. The addition of fibers decreases the density, due to the increase in air void content. Among the pastes with different types of fiber surface condition, the density is higher, and the air void content is lower, whether the silica fume is as-received or silane-treated. Correlation with the results on the effect of fiber surface condition on the tensile strength and modulus (Section B) shows that the higher is the density, the higher the tensile strength and modulus. A higher modulus is probably due to a better bond between fiber and matrix. Hence, a better fiber-matrix bond results in a lower air void content, which in turn results in a higher density. Silane treatment of silica fume has negligible effect on the density, though the air void content is significantly decreased. This is attributed to the low density of silane.

Silica fume decreases the thermal conductivity of cement paste (Table 15) because of the decreases in thermal diffusivity (Table 13) and density (Table 14). The thermal conductivity is decreased in spite of the increase in the specific heat. Among the cement pastes with different fiber surface conditions, a higher thermal conductivity is associated with a higher thermal diffusivity. In other words, for carbon fiber cement pastes, the thermal diffusivity influences the thermal conductivity more than either the density or the specific heat.

Although the carbon fibers are quite conductive, their low concentration causes the thermal conductivity of cement paste to increase slightly. By using silane-treated carbon fibers, the thermal conductivity increase due to the fiber addition is even less.For practical applications, a high specific heat and a low thermal conductivity are desired. By using silane-treated carbon fibers and silane-treated silica fume, both properties are attained. Relative to plain cement paste, the specific heat is 12% higher and the thermal conductivity is 40% lower.

REDUCING DRYING SHRINKAGE OF CEMENT PASTE BY ADMIXTURE SURFACE TREATMENT

The drying shrinkage of concrete during curing is a source of residual stress and cracks. The problem is particularly severe for a large structure, such as a large concrete floor. Various admixtures such as silica fume,[3,16,31] carbon fibers,[16,23,32,33] and liquid chemicals[34-36] have been used to reduce the drying shrinkage. The effect of admixture surface treatment on the drying shrinkage, however, has not been previously investigated. In this section, it is reported that the surface treatment of an admixture is effective for enhancing the usefulness of the admixture in reducing the drying shrinkage.

Experimental methods and materials

Material sources and preparation methods are as described in Section B.

Drying shrinkage measurements were conducted as a function of curing age on samples 280 x 25.4 x 25.4 mm in size. A stainless steel contact point was positioned at each end along the length of each sample, such that the exterior tips of the two contact points were outside the sample and the interior tips of the two contact points were inside the sample and were separated by a distance of 250 mm, which was the gage length for drying shrinkage strain measurement. The measurement was conducted in accordance with ASTM method C 490-93a.

Ten compositions, as listed in Table 16, were studied. Five of them had as-received silica fume; the other five had silane-treated silica fume.

Results

Table 16 gives the drying-shrinkage strain of 10 types of cement paste as a function of curing age. The drying shrinkage is decreased by the addition of carbon fibers, such that it decreases in the following order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies for any curing age, whether the silica fume is as-received or silane-treated. The drying shrinkage is decreased by the use of silane-treated silica fume in place of as-received silica fume, whether or not fibers are present. The drying shrinkage strain at 28 days is decreased by 5% when fibers are absent and silane-treated silica fume is used in place of as-received silica fume. When silane-treated fibers are present, it is decreased by 10% when silane-treated silica fume is used in place of as-received silica fume. By adding silane-treated fibers to the paste with as-received silica fume, the shrinkage at 28 days is decreased by 25%. By adding silane-treated fibers to the paste with silane-treated silica fume, the shrinkage at 28 days is decreased by 28%. By adding silane-treated fibers and replacing as-received silica fume by silane-treated silica fume, the shrinkage at 28 days is decreased by 32%.

Discussion

Carbon fiber addition is effective for decreasing the drying shrinkage, as previously reported.[16,23,32,33] The effectiveness is further enhanced by surface treatment of the fibers. The greater effectiveness of silane treatment compared to the other fiber surface treatments for drying shrinkage reduction is consistent with its greater effectiveness for improving the mechanical properties (Sections B and C), decreasing the air void content (Section B), and increasing the specific heat (Section D). The effectiveness of silane treatment for both fibers and silica fume is partly attributed to the hydrophylic nature of silane. The hydrophylic nature is expected to enhance the admixture dispersion. A higher degree of admixture dispersion is expected to reduce the drying shrinkage. In addition, the enhanced bond between admixture and cement matrix due to the silane covalent coupling is expected to result in a reduction of the drying shrinkage. The combined use of silane-treated silica fume and silane-treated carbon fibers is most effective.

CONCLUSION

The surface treatment of silica fume by a silane coupling agent prior to incorporation in mortar was found to greatly enhance the consistency of the silica fume mortar mixture and to cause the tensile strength to increase by 31% and the compressive strength to increase by 27%, relative to the values obtained without treatment. The effect on slump is due to the enhanced wetability of silica fume by water. The effect on strength is due to improved bond between silica fume and cement and to increased density of the mortar. It may also be due to the improved dispersion of silica fume. In addition, the silane treatment resulted in increases in tensile and compressive moduli, and in flexural storage modulus and loss tangent. The tensile strength, modulus, and ductility were increased and the air void content was decreased when the fibers in carbon fiber-reinforced cement paste had been surface treated. The effectiveness of treatment decreased in the following order: silane, dichromate, and ozone. Additional strengthening and air void content reduction were observed when the silica fume in the carbon fiber-reinforced cement paste had been surface treated with silane. These effects of silane treatment are attributed to the hydrophylic nature of silane.

The addition of carbon fibers (0.5% by weight of cement) to

Table 16—Drying-shrinkage strain (10^{-4}, ± 0.015) at different curing ages

	With as-received silica fume				With silane-treated silica fume			
Formulation	1 day	4 days	8 days	28 days	1 day	4 days	8 days	28 days
B	1.13	3.02	3.72	4.41	1.01	2.88	3.62	4.18
BF	0.83	2.42	3.05	3.51	0.78	2.25	2.81	3.19
BO	0.83	2.36	3.02	3.48	0.76	2.24	2.79	3.09
BK	0.82	2.32	3.02	3.48	0.76	2.23	2.79	3.09
BS	0.81	2.32	2.98	3.31	0.75	2.12	2.72	2.99

B: cement + water + water-reducing agent + silica fume + methylcellulose + defoamer.
BF: B + as-received fibers.
BO: B + O_3-treated fibers.
BK: B + dichromate-treated fibers.
BS: B + silane-treated fibers.

cement paste containing silica fume (15% by weight of cement) and methylcellulose (0.4% by weight of cement) caused the loss tangent under flexure to decrease by up to 25% and the storage modulus to increase by up to 67%, such that both effects depended on the fiber surface treatment and increased in the following order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers. The addition of methylcellulose to cement paste containing silica fume (but no fiber) caused the loss tangent to increase by up to 50% and the storage modulus to decrease by up to 14%. Silane treatment of silica fume had little effect on the loss tangent, but increased the storage modulus by up to 38%.

The specific heat of cement paste was increased by 12% and the thermal conductivity was decreased by 40% by using as admixtures silane-treated silica fume and silane-treated carbon fibers. The effects were less when the silica fume was as-received or when the fibers were as-received, ozone-treated, or dichromate-treated.

The specific heat was increased by the carbon fiber addition, due to fiber-matrix interface slippage. The increase was in the following order: as-received fibers, ozone-treated fibers, dichromate treated fibers, and silane-treated fibers. The increase in specific heat due to the silane treatment of the fibers is attributed to the movement of the silane molecules. The increase in specific heat due to the dichromate or ozone treatment of the fibers is attributed to the movement of the functional groups on the fibers. The specific heat was increased by the silica fume addition, due to the slippage at the interface between silica fume and cement. The increase was enhanced by silane treatment of the silica fume.

Silane treatment of carbon fibers decreased the thermal conductivity in spite of the increases in specific heat and density. This is due to the decrease in thermal diffusivity, which is attributed to the thermal resistance of the silane at the fiber-matrix interface. Dichromate and ozone treatments of carbon fibers gave higher thermal diffusivity than silane treatment of the fibers, due to the functional groups on the fiber surface strengthening the fibermatrix interface.

Silane treatment of silica fume and carbon fibers was highly effective for decreasing the drying shrinkage of cement paste. By adding silane-treated carbon fibers and replacing as-received silica fume by silane-treated silica fume, the shrinkage at 28 days was decreased by 32%. Silane treatment of fibers was more effective than dichromate treatment or ozone treatment.

REFERENCES

1. Sabir, B. B., "High-Strength Condensed Silica Fume Concrete," *Magazine of Concrete Research*, V. 47, 1995, pp. 219-226.

2. Toutanji, H. A., and El-Korchi, T., "Tensile and Compressive Strength of Silica Fume-Cement Pastes and Mortars," *Cement, Concrete, and Aggregates*, V. 18, 1996, pp. 78-84.

3. Haque, M. N., "Strength Development and Drying Shrinkage of High-Strength Concretes," *Cement and Concrete Composites*, V. 18, 1996, pp. 333-342.

4. Chen, P.-W., and Chung, D. D. L., "Concrete Reinforced with up to 0.2 vol.% of Short Carbon Fibers," *Composites*, V. 24, No. 1, 1993, pp. 33-52.

5. Shi, Z.-Q., and Chung, D. D. L., "Improving the Abrasion Resistance of Mortar by Adding Latex and Carbon Fibers," *Cement and Concrete Research*, V. 27, No. 8, 1997, pp. 1149-1153.

6. Bürge, T. A., "Densified Cement Matrix Improves Bond with Reinforcing Steel," *Bond in Concrete*, P. Bartos, ed., pp. 273-281, Applied Science Publishers, London, 1982.

7. Gjørv, O. E.; Monteiro, P. J. M.; and Mehta, P. K., "Effect of Condensed Silica Fume on the Steel-Concrete Bond," *ACI Materials Journal*, V. 87, No. 6, Nov.-Dec. 1990, pp. 573-580.

8. Cabrera, J. G., and Claisse, P. A., "Measurement of Chloride Penetration into Silica Fume Concrete," *Cement and Concrete Composites*, V. 12, 1990, pp. 157-161.

9. Luther, M. D., "Silica-Fume (Microsilica) Concrete in Bridges in the United States," *Transportation Research Record*, V. 1204, 1988, pp. 11-20.

10. Bubshait, A.A.; Tahir, B. M.; and Jannadi, M.O., "Use of Microsilica in Concrete Construction," *Building Research Information*, V. 24, No. 1, 1996, pp. 41-49.

11. Punkki, J.; Golaszewski, J.; and Gjørv, O. E., "Workability Loss of High-Strength Concrete," *ACI Materials Journal*, V. 93, No. 5, Sept.-Oct. 1996, pp. 427-431.

12. Li, X., and Chung, D. D. L., "Improving Silica Fume for Concrete by Surface Treatment," *Cement and Concrete Research*, V. 28, No. 4, 1998, pp. 493-498.

13. Xu, Y., and Chung, D. D. L., "Increasing Thermal Conductivity of Boron Nitride and Aluminum Nitride Particle Epoxy-Matrix Composites by Particle Surface Treatments," *Composite Interfaces*, in press.

14. Chen, P.-W., and Chung, D. D. L., "Carbon-Fiber-Reinforced Concrete as a Smart Material Capable of Non-Destructive Flaw Detection," *Smart Materials and Structures*, V. 2, 1993, pp. 22-30.

15. Fu, X.; Lu, W.; and Chung, D. D. L., "Improving Tensile Properties of Carbon-Fiber-Reinforced Cement by Ozone Treatment of the Fiber," *Cement and Concrete Research*, V. 26, No. 10, 1996, pp. 1485-1488.

16. Chen, P.-W., and Chung, D. D. L., "Low-Drying-Shrinkage Concrete Containing Carbon Fibers," *Composites*, Part B, V. 27B, 1996, pp. 269-274.

17. Chen, P.-W., and Chung, D. D. L., "A Comparative Study of Concretes Reinforced with Carbon, Polyethylene, and Steel Fibers and Their Improvement by Latex Addition," *ACI Materials Journal*, V. 93, No. 2, Mar.-Apr. 1996, pp. 129-133.

18. Chen, P.-W., and Chung, D. D. L., "Concrete as a New Strain/Stress Sensor," *Composites*, Part B, V. 27B, 1996, pp. 11-23.

19. Fu, X., and Chung, D. D. L., "Self-Monitoring of Fatigue Damage in Carbon-Fiber-Reinforced Cement," *Cement and Concrete Research*, V. 26, No. 1, 1996, pp. 15-20.

20. Chen, P.-W.; Fu, X.; and Chung, D. D. L., "Microstructural and Mechanical Effects of Latex, Methylcellulose and Silica Fume on Carbon-Fiber-Reinforced Cement," *ACI Materials Journal*, V. 94, No. 2, Mar.-Apr. 1997, pp. 147-155.

21. Hou, J., and Chung, D. D. L., "Cathodic Protection of Steel Reinforced Concrete Facilitated by Using Carbon-Fiber-Reinforced Mortar or Concrete," *Cement and Concrete Research*, V. 27, No. 5, 1997, pp. 649-656.

22. Fu, X.; Ma, E.; Chung, D. D. L.; and Anderson, W. A., "Self-Monitoring in Carbon-Fiber-Reinforced Mortar by Reactance Measurement," *Cement and Concrete Research*, V. 27, No. 6, 1997, pp. 845-852.

23. Banthia, N., "Carbon Fiber Cements: Structure, Performance, Applications and Research Needs," *Fiber Reinforced Concrete*, SP-142, J. I. Daniel, and S. P. Shah, eds., American Concrete Institute, Farmington Hills, Mich., 1994, pp. 91-119.

24. Toutanji, H. A.; El-Korchi, T.; and Katz, R. N., "Strength and Reliability of Carbon-Fiber-Reinforced Cement Composites," *Cement and Concrete Composites*, V. 16, 1994, pp. 15-21.

25. Soroushian, P.; Nagi, M.; and Hsu, J., "Optimization of Use of Lightweight Aggregates in Carbon Fiber-Reinforced Cement," *ACI Materials Journal*, V. 89, No. 3, May-June 1992, pp. 267-276.

26. Sakai, H.; Takahashi, K.; Mitsui, Y.; Ando, T.; Awata, M.; and Hoshijima, T. "Flexural Behavior of Carbon Fiber-Reinforced Cement Composite," *Fiber Reinforced Concrete*, SP-142, J. I. Daniel, and S. P. Shah, eds., American Concrete Institute, Farmington Hills, Mich., 1994, pp. 121-140.

27. Fu, X., Lu, W., and Chung, D. D. L., "Ozone Treatment of Carbon Fiber for Reinforcing Cement," *Carbon*, V. 36. No. 9, 1998, pp. 1337-1345.

28. Fu, X.; Li, X.; and Chung, D. D. L., "Improving the Vibration Damping Capacity of Cement," *Journal of Materials Science*, V. 33, 1998, pp. 3601-3605.

29. Wang, Y., and Chung, D. D. L., "Effects of Sand and Silica Fume on the Vibration Damping Behavior of Cement," *Cement and Concrete Research*, V. 28, No. 10, 1998, pp. 1353-1356.

30. Fu, X., and Chung, D. D. L., "Effects of Silica Fume, Latex, Methylcellulose, and Carbon Fibers on the Thermal Conductivity and Specific Heat of Cement Paste," *Cement and Concrete Research*, V. 27, No. 12, 1997, pp.1799-1804.

31. Al-Khaja, W. A., "Strength and Time-Dependent Deformations of Silica Fume Concrete for Use in Bahrain," *Construction Building Materials*, V. 8, No. 3, 1994, pp. 169-172.

32. Ohama, Y., "Carbon-Cement Composites," *Carbon*, V. 27, No. 5, 1989, pp. 729-737.

33. Park, S. B., and Lee, B. I. "Mechanical Properties of Carbon-Fiber-Reinforced Polymer Impregnated Cement Composites," *Cement and Concrete Composites*, V. 15, No. 3, 1993, pp. 153-163.

34. Balogh, A., "New Admixture Combats Concrete Shrinkage," *Aberdeen's Concrete Construction*, V. 41, No. 7, 1996, pp. 546-551.

35. Shah, S. P.; Weiss, W. J.; and Yang, W., "Shrinkage Cracking—Can It Be Prevented?" *Concrete International*, V. 20, No. 4, Apr. 1998, pp. 51-55.

36. Nmai, C. K.; Tomita, R.; Hondo, F.; and Buffenbarger, J., "Shrinkage-Reducing Admixtures," *Concrete International*, V. 20, No. 4, Apr. 1998, pp. 31-37.