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Carbon fiber reinforced cement improved by using silane-treated carbon fibers

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Abstract

The tensile strength of cement paste was increased by 56% and the modulus and ductility were increased by 39% by 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 about equally to the strengthening. Silane treatment of fibers and silica fume also decreased the air void content. The 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. Silane's effectiveness is due to its hydrophilic nature.

Keywords: Fiber reinforcement; Cement paste; Tensile properties; Silica fume; Silane

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 [1–12]. Surface treatment of carbon fibers by ozone has been shown to be effective for improving the wettability 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 [13]. We have recently reported that the surface treatment of silica fume by using a silane-coupling agent improves both workability and strengths (tensile and compressive) of cement mortar beyond the levels attained by using untreated silica fume, due to the hydrophilic nature of the silane molecule and the consequent improved wettability of silica fume by water [14]. In this paper, we report 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.

Silica fume is commonly used along with carbon fibers in order to help the dispersion of the fibers in the cement mix [5]. In this paper, we also report 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.

1. Experimental methods

The carbon fibers were isotropic pitch based, unsized, and of length ~5 mm, as obtained from Ashland Petroleum Co. (Ashland, Kentucky, USA). The fiber properties are shown in Table 1. As-received and three types of surface-treated fibers were used. The fiber content was 0.5% by weight of cement. The surface treatments involved (a) ozone (O_3), (b) an aqueous solution of potassium dichromate ($K_2Cr_2O_7$, 30 wt.%), sulfuric acid (H_2SO_4, 40 wt.%, which enhances the oxidation ability), and (c) 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 minutes. Prior to O_3 exposure, the fibers had been dried at 160°C in air for 30 minutes. The potassium dichromate treatment for surface oxidation involved immersion in the dichromate solution and heating to 60°C while stirring for 2 hours, followed by filtration and washing with water and then drying at 110°C for 6 hours. For the silane treatment, the silane coupling agent was a 1:1 (by weight) mixture of Z-6020 ($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH)_3)_3$) and Z-6040 ($OCH_2CHCH_2OCH_2CH_2CH_2Si(OCH)_3)_3$) from Dow Corning Corp. (Midland, MI, USA). The amine group in Z-6020

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Table 1
Propeties of carbon fibers

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

serves as the catalyst for the curing of epoxy and consequently allows the Z-6020 molecule to attach to the epoxy end of the Z-6040 molecule. The trimethylsiloxy ends of the Z-6020 and Z-6040 molecules then connect to the -OH functional group on the surface of silica fume or carbon fibers. The silane was dissolved in ethylacetate. Surface treatment was performed by immersion in the silane solution, heating to 75°C while stirring, and holding at 75°C for 1 hour, followed by filtration, washing with ethylacetate, and drying. After this, heating was conducted in a furnace at 110°C for 12 hours.

No aggregate (fine or coarse) was used. The water/cement ratio was 0.35. A water-reducing agent (TAMOL SN, Rohm and Haas Co., Philadelphia, PA, USA; sodium salt of a condensed naphthalenesulphonic acid) was used in the amount of 2% by weight of cement.

The cement used was portland cement (type I) from Lafarge Corp. (Southfield, MI, USA). The silica fume (Elkem Materials, Inc., Pittsburgh, PA, USA, EMS 965) was used in the amount of 15% by weight of cement. The methylcellulose, used in the amount of 0.4% by weight of cement, was from Dow Chemical (Midland, MI, USA, Methocel A15-LV). The defoamer (Colloids Inc., Marietta, GA, USA, 1010) was used whenever methylcellulose was used in the amount of 0.13 vol.%.

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 minutes. Then this mixture (if applicable), cement, water, water reducing agent, silica fume, and fibers (if applicable) were mixed in the mixer for 10 minutes. After pouring into molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 hours and then cured in air at room temperature and a relative humidity of 100% for 28 days.

Dog-bone shaped specimens of the dimensions shown in Fig. 1 from Fu et al. [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 (Sintech 2/D, Research Triangle Park, NC, USA). The displacement rate was 1.27 mm/min. 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 2, 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.

2. Results

Tables 2 and 3 show the tensile strength and modulus, respectively, of twelve 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. However, both strength and modulus are increased by the addition of fibers. The effectiveness of the fibers in increasing strength and modulus increases in the 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 of fibers are about equally valuable in providing strengthening.

Table 4 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 effec-

Table 2
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	3.12 ± 0.12

* A, cement + water + water reducing agent + silica fume; A^+, A + methylcellulose + 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 3
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

* Abbreviations as in Table 2.

Table 4
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

* Abbreviation as in Table 2.

Table 5
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

* Abbreviations as in Table 2.

tiveness of the fibers in increasing the ductility increases in the 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 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 pate 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 5 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 the fibers have been surface-treated or not. Among the formulations with fibers, the air void content decreases in the 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.

3. Discussion

The hydrophilic nature of the silane molecule is believed to improve the bond between fiber and cement paste or that 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 hydrophilicity. 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. Although the silane treatment has previously been used for silica fume [14], it has not been used for carbon fibers for use in cement. Moreover, the effect of silane treatment of silica fume on the air void content of cement paste has not been previously investigated. 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.

4. Conclusion

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 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 hydrophilic nature of silane.

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